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TECHNOLOGICAL CHARACTERISTICS OF MANUFACTURING ARTICLES WITH A COMPLICATED SHAPE FROM PETROSITAL

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The technological characteristics of manufacturing articles with a complex shape from petrosital by means of thermoplastic pressing from cast slips of two types — fused basalt (glass) – plasticizer and natural basalt – basalt glass – plasticizer — are investigated. It is shown that the energy-intensiveness of the technological process can be decreased by minimizing the content of the glass component of the composition without harming the technological characteristics of the casting slip or the physical – chemical properties of the petrosital.

Key words: petrosital, thermoplastic technology, basalt, casting slip, phase state, anortite, hematite, spherical elements, structure, heat-treatment, energy conservation.

Different industrial applications of glass ceramic materials for manufacturing articles which operate under the combined effect of corrosive media and different kinds of friction have been under intensive investigation in recent years. Specifically, transporting facilities whose units and parts operate under complex conditions of corrosion and abrasion, giving rise to rapid wear of individual parts and failure, are widely used in enterprises of the petrochemical complex.

Scarce alloyed steels are the main material used for fabricating the critical parts of equipment, for example, specific elements of locking devices. However, their cost has risen sharply in recent years. Together with two of their negative characteristics — relatively low resistance to mechanical actions and chemical corrosion — this makes it important to use for such purposes two types of materials, for example, glass ceramics, which possess high compression strength, hardness, resistance to the action of melts of salts, slags, and metals, and corrosive liquids and gases as well as the action of temperature, which makes it possible to use them in chemical and metallurgical industries, casting, and elsewhere.

The main objective of the present work is to develop a composition and technology for obtaining glass ceramic articles with complex shape which resist abrasive wear and corrosion.

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The local problems which need to be solved were: choice of initial material for preparing the casting slip and the production method, designing the press mold, and determining the engineering parameters of the production process which ensure a long service life for the parts. Important requirements for the processes being developed are cost-effectiveness and ecological safety.

Basalt from the Rovenskoe deposit (Ukraine), being accessible and inexpensive and distinguished by the stability of the chemical-mineral composition, was chosen as the initial material base for obtaining glass ceramics.

Taking account of the complexity of the configuration and preciseness of the dimensions of the spherical elements obtained, the thermoplastic method of formation followed by heat treatment, which facilitates crystallization and sintering of the articles, was chosen from among the existing methods of production [1 – 5].

During heat treatment, the plasticizer (paraffin) is removed, compaction occurs, and the required strength of the articles is attained as a result of liquid-phase sintering and crystallization of the pyroxene phases, which have high physical – chemical parameters.

The thermoplastic technology for obtaining parts on the basis of basalt was altered to make the process more efficient. Specifically, the fraction of fused basalt (glass) in the initial mix, used as a high-temperature binder, was reduced to a minimum. The remaining part of the mix consisted of

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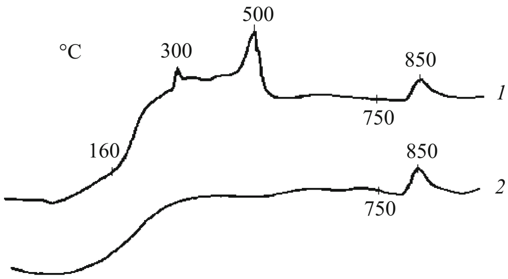

Fig. 1. DTA curves of finely milled glass based on basalt with (*1*) and without (*2*) binder (paraffin).

TABLE 1.

Heat-treatment temperature, °C	Physical – chemical properties of the samples		
	water absorption, %	apparent density, kg/m^3	open porosity, %
750	16.54	1909	31.58
850	11.37	2105	23.93
950	10.64	2186	22.44
1000	8.85	2208	19.54
1050	7.87	2268	17.84
1100	0.12	2758	0.33

natural basalt. In other words, a partial transition was made from the glass technology for obtaining articles to a ceramic technology; this makes it possible to decrease the energy-intensiveness of production substantially.

The average chemical composition of the basaltic rock is as follows (wt.%): 48.96 $SiO_2$15.13 Al_2O_3, 2.83 TiO_2, 14.87 Fe_2O_3, 4.38 MgO, 9.53 CaO, 3.53 R_2O ($Na_2O + K_2O$). The mineral composition of the initial basalt according to x-ray phase analysis is represented by anortite and pyroxene materials — augite and diopside. A small quantity of palagonite rock — a mixture of minerals form the chlorite and chlorophaeite group — is present [6].

To form articles by the thermoplastic method a fluid slip must be prepared using a plasticizer (paraffin) and fed under pressure 0.5 – 0.6 MPa into a compression mold placed on a metal stand and through a system of pouring gates, set the shape of the article by cooling the blank, disassemble the mold, and remove the article. A preliminary study of the volume changes of molded samples occurring in course of heat treatment showed that the total volume shrinkage of the material was equal to 12.8%, which was taken into account when the mold was designed. As a result of the spherical shape of the articles, the construction of the compression mold was complex and the mold was designed with the aid of a computer.

An integral part of the thermoplastic technology is preparing the initial components of the basalt and glass powders with specific surface area 5000 – 6000 cm^2/g. To obtain petrosital special attention must be given to making the correct choice of temperatures for burning out the binder as well as for crystallization and sintering of the material.

The glass component of the mix was synthesized by making comminuted fused basalt in a gas furnace at 1450°C followed by granulation in water, drying, and milling in a vibratory mill.

Since the sintering of the material depends practically completely on the onset temperature of softening of the glassy component, a differential-thermal analysis of the finely milled basalt glass as well as its composition with the binder was performed (Fig. 1).

The DTA curve of the mix with the binder is more complex and shows substantially differences from the DTA curve of the initial glass. In the temperature range 160 – 550°C the DTA curve exhibits several exothermal effects, which are associated with the burn-out of the binder. It is well known that paraffin is a complex mixture of hydrocarbons with different molecular mass, and the light fractions, which are present in very large amounts, burn out in the temperature interval 160 – 300°C. The medium-weight fractions, whose content is low, are removed in the temperature in interval 320 – 470°C. The strongest exothermal effect, occurring at 500°C, is due to burn-out of a large quantity of heavy fractions. Since the intense release of gas accompanying the removal of the thermoplastic binder can result in cracking and shape loss of the sample, the behavior of the sample during heating was studied and the following temperature – time parameters for heat-treatment of the molded blanks for the articles were adopted:

rate of temperature increase less than 2 K/min in the temperature interval 50 – 550°C;

soaking at 200°C for 0.5 h; and,

soaking at 470°C for 0.5 h.

Since the course of both DTA curves in the temperature interval 550 – 1000°C is identical and an exothermal effect due to the formation of the pyroxene phase is observed at 850°C, the crystallization of the samples is not accompanied by strong volume changes, which makes it possible to increase the temperature rapidly (up to 300 K/h) from 550°C to the final kilning temperature.

Two compositions were used to prepare the casting mix: one was prepared on the basis of basaltic glass and the other from two components — basalt and glass. The change of the physical – chemical properties of the samples which were obtained with heat-treatment in the interval 750 – 1100°C (the temperature step was 100°C from 750 to 950°C and 50°C in the interval 100 – 1100°C) was studied to choose the final kilning temperature.

The physical – chemical properties of the heat-treated samples which were obtained from the casting mix based on the basaltic glass powder are presented in Table 1.

Evidently, the indicators of the properties studied change little up to temperature 1050°C. In the temperature interval 1050 – 1100°C water absorption and porosity decrease sharply and the apparent density increases as a result of the

TABLE 2.

Heat-treatment temperature, °C	Physical – chemical properties of the samples			
	water absorption, %	apparent density, kg/m^3	open porosity, %	shrinkage, %
920	25.2	1678	42.28	0.907
970	25.7	1673	42.98	0.725
1020	25.2	1688	42.61	1.269
1070	17.2	1879	32.29	3.626
1120	4.1	2461	10.90	9.338

intense sintering, which is practically completed by 1100°C, which is the final kilning temperature. The articles were soaked at this temperature for 1 h.

The main crystalline phases in the synthesized material are anortite, augite, and hematite, whose characteristic peaks are presented below.

Crystalline phase	Main diffraction peaks, nm
Anortite $Ca(Si_2Al_2O_8)$	0.326, 0.320, 0.318, 0.312, 0.295, 0.252
Augite $Ca(Mg, Al, Fe)Si_2O_6$	0.299, 0.255, 0.335, 0.255, 0.162
Hematite α-Fe_2O_3	0.269, 0.251, 0.184

An investigation of the regularities in the changes of the physical – chemical properties and phase composition as a function of the heat-treatment temperature showed that three main kilning stages can be identified for samples obtained by molding from a casting mix of basaltic glass: 700 – 850°C — molding of the crystalline phase, onset of sintering due to residual glass phase; 850 – 1050°C — growth of crystals and increase in the amount of the crystalline phase; and, 1050 – 1100°C — intensification of sintering.

The samples kilned at 1100°C (soaking 1 h) were characterized by lowest water absorption and porosity and high apparent density, making it possible to take this as the optimal temperature.

Thus, basaltic glass can be used as a base for obtaining samples with a complex shape from glass crystal material using thermoplastic molding. A substantial drawback of this technological process is the need for a glassmaking stage, which is an energy-intensive process. For this reason, replacing the maximum possible amount of glass with finely comminuted natural basalt will decrease the energy consumption considerably.

The initial glass was comminuted to fineness 4500 – 5000 cm^2/g and mixed with finely comminuted basalt (specific surface area 7000 – 8000 cm^2/g) in various ratios.

Subsequently, the experimental samples were obtained with temperature increasing to 550°C at the same rates that were used for heat-treatment of the glass – paraffin composition.

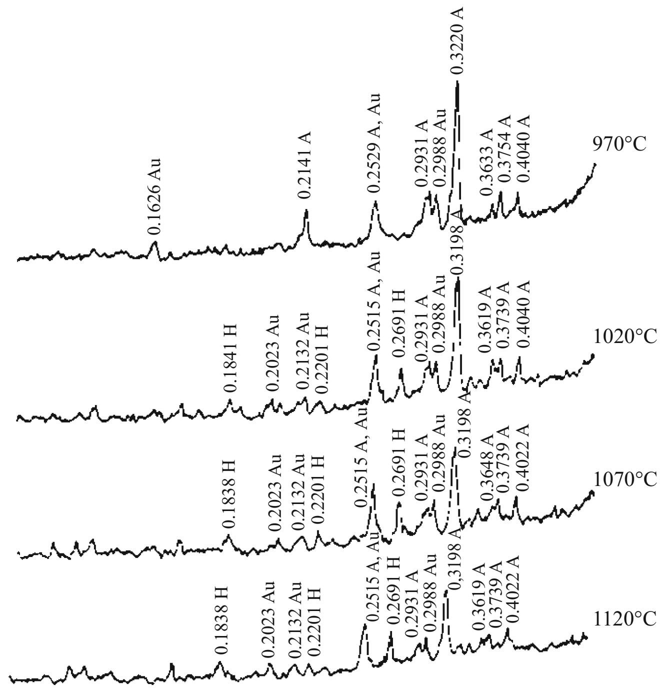

Fig. 2. X-ray diffraction patterns of heat-treated basalt – glass compositions: A) anortite; Au) augite; H) hematite.

On the basis of the results of the investigation the temperature interval 920 – 1120°C was chosen to study structure formation and the phase composition of the synthesized materials. The heat-treatment regime after 550°C was as follows: heating of the basalt – glass composite at the rate 300 K/h to the final temperature → soaking 1 h → inertial cooling. The physical – chemical properties of the heat-treated samples were investigated (Table 2).

Analysis of the dependences of the physical – chemical properties of the samples presented in Table 2 on the heat-treated temperature led to the conclusion that glass ceramic articles are obtained in two stages.

A small decrease of the porosity and water absorption and increase of the apparent density are observed at the first stage (920 – 1070°C). This is due to, first and foremost, sintering onset as a result of the high-viscosity glass phase introduced as a binder.

At the second state (1070 – 1120°C) sintering intensifies and is completed. This is accompanied by a sharp decrease of the water absorption and porosity as well as an increase of the apparent density and shrinkage. The material acquires a dense structure, the number of pores decreases sharply, and the mechanical strength increases. However, when temperature 1120°C is reached the water absorption is 4.1% and the open porosity 10.09%, which indicates that the sintering of the material is not completed. A further increase of the temperature results in swelling and deformation of the samples, so that the soaking at the final kilning temperature was increased to 2 h to obtain a denser structure of the material.

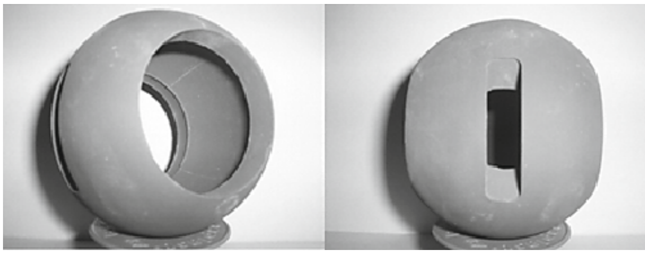

Fig. 3. Spherical elements of locking devices manufactured from pertrosital.

Increasing the heat-treatment temperature to 1200°C results in the appearance of a new crystalline phase — hematite, which is not identified in the initial basalt, but it is formed during crystallization of basaltic glass. In addition, the intensity of the diffraction peaks of anortite and augite decreases appreciably, which could be due to the partial melting of basalt. Evidently, at 1120°C the smallest grains transition into the glass phase, which, as it increases in quantity, intensifies sintering.

In obtaining articles from petrositals by thermoplastic molding based on a basalt – glass composition, two basic temperature stages in glass crystal formation can be identified:

920 – 1170°C — sintering onset due to the liquid glass phase (binder) and change of the phase composition of the material;

1070 – 1120°C — sintering intensification and melting of small anortite and augite crystals.

The optimal heat-treatment temperature at which the maximum level of the main engineering and operating characteristics of the material are attained was determined to be 1120°C (soaking 2 h).

The spherical elements of locking devices, fabricated by thermoplastic molding followed by heat-treatment, are presented in Fig. 3. The articles have a dense uniform sital structure with no signs of deformation.

The properties of the petrositals obtained using thermoplastic technology with optimal heat-treatment are presented in Table 3.

The chemical stability, durability, and impact toughness indicators make it possible to classify petrositals as wear-resistant materials. Glass ceramics based on a basalt – glass composition are at least as good as petrositals based on basaltic glass with respect to the mechanical properties; this is explained by the fact that the phase composition, which is represented by anortite, augite, and hematite, is identical.

The results obtained make it possible to recommend synthesized glass crystal materials for obtaining articles with a complex configuration which operate in aggressive media and under different kinds of friction.

Articles were fabricated from petrosital with a prescribed system of physical – chemical properties by means of an energy-conserving technology using a mix composition consisting of natural basalt and basaltic glass, the first component being the predominant.

TABLE 3.

Indicator	Petrosital based on	
	basalt – glass composition	basaltic glass
Heat-treatment temperature,* °C	1120	1100
CLTE, 10^{-7} K^{-1} in the temperature interval 20 – 300°C	75.9	78.5
Acid resistance in 1 N HCl, %	96.7	96.2
Apparent density, kg/m^3	2690	2758
Open porosity, %	0.12	0.33
Water absorption, %	0.06	0.12
Shrinkage, %	9.3	9.5
Abrasion losses, g/cm^2	0.032	0.030
Impact toughness, kJ/m^2	3.10	2.91

* Soaking 2 h.

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